evidence in general, however, supports the expectation that fields which push the electrons away from the metal cathode into the germanium produce larger signals and some extension of the spectral response. Figure 2 shows some particularly good data illustrating these field effects.

With the present electroplated tin-on-germanium specimens, the spectral responses extend to about 3.4 microns. The quantum yields are typically a few tenths of a percent, and significant improvement in these yields may be anticipated. In principle, potential barriers between solids may be very small, and thus photoemission at much longer wavelengths may be ultimately achieved.

[1] N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Oxford University Press, New York, 1940), pp. 73, 173.
[2] M. A. Gilleo, Phys. Rev. 91, 534 (1953).
[3] R. Williams and R. H. Bube, J. Appl. Phys. 31, 968 (1960).
[4] See, e.g., T. S. Moss and T. D. H. Hawkins, Phys. Rev. Letters 1, 129 (1958).

NUCLEAR MAGNETIC RESONANCE OF Cr53 IN ANTIFERROMAGNETIC CrCl3†

A. Narath
Sandia Corporation, Albuquerque, New Mexico
(Received November 6, 1961)

The metamagnetic properties of the anhydrous iron group chlorides have been the subject of many investigations in the past. Recently, several of these hexagonal layer type compounds were shown to become antiferromagnetic at low temperatures.[1] The magnetic ordering consists of ferromagnetically aligned moments within each hexagonal layer. The antiferromagnetic coupling between adjacent layers is relatively weak and as a consequence steep net magnetization curves are obtained even for small external magnetic fields.[2] This effect suggests that an enhancement mechanism similar to that found in ferromagnets[3] might make it feasible to measure the temperature dependence of the sublattice magnetization in some of these compounds by nuclear magnetic resonance (NMR) techniques.

In this Letter we wish to report the observation of the Cr53 NMR in CrCl3 in the temperature range of 1.23°K-4.02°K and zero external field. Results of precision measurements of the frequency for resonance are in excellent agreement with the predictions of simple spin-wave theory for a two-dimensional ferromagnetic system in the presence of anisotropy.

CrCl3 has a hexagonal unit cell, of space group D_3^5, containing 6 molecules.[4] It exhibits a λ-type specific heat anomaly at 16.8°K[5] and a magnetic susceptibility maximum around 20°K. Neutron diffraction studies[6] give an ordered structure in which the axes of magnetization are directed per-

pendicular to the c axis. Polycrystalline samples for the present study were prepared by vacuum sublimation of the dehydrated salt at 700°C. The nuclear resonance spectra are sensitive to the crystallographic purity of the samples. Resonances in addition to those reported here were observed in samples which exhibited a large number of stacking faults and other imperfections.

The resonance was observed with a frequency-swept FM marginal oscillator.[7] As in the case of ferromagnetic CrBr3,[8] the spectrum consists of a well-resolved triplet due to a nuclear electric quadrupole interaction. From the separation of the satellites, $I = \frac{3}{2}$, and the assumption that the electric field gradient at the Cr positions has cylindrical symmetry about the c axis, we obtain $h^{-1}e^2q_{zz}Q = 0.882 \pm 0.010$ Mc/sec. The central component of the spectrum is shifted by the second order effect to slightly higher frequency (~ 6 kc/sec) relative to the satellites. This shift agrees in magnitude and direction with the previous assumptions.

A comparison of the intensities of the Cr53 resonances in CrBr3 and CrCl3 showed that the enhancement factor in these two compounds is of the same order of magnitude. However, since the quadrupole splitting in CrCl3 is insensitive to the orientation of the magnetization in the hexagonal plane it is not yet certain whether the resonance is excited by domain rotation or domain wall displacement. The observed linewidths are
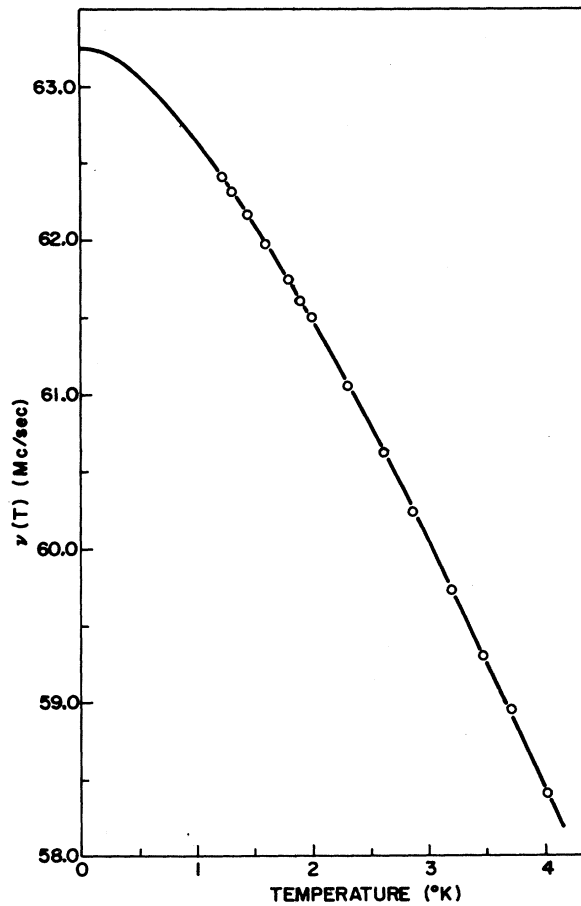
FIG. 1. Temperature dependence of the Cr^{53} NMR (central component) in $CrCl_3$, in zero external field. Solid curve shows the best fit to the data by the two-dimensional spin-wave model.

rather large (~100 kc/sec) and may be caused by a distribution of magnetic dipole fields resulting from imperfect antiferromagnetic order.

In Fig. 1 we show the temperature dependence of the Cr^{53} NMR. If we make the usual assumption that the hyperfine coupling constant does not depend on temperature the observed frequencies are proportional to the sublattice magnetization. The variation of the frequencies is almost linear in temperature and hence cannot be fitted to a T^2 departure $(T_{AE} < T \ll T_N)$ or an exponential departure $(T < T_{AE})$ predicted for an antiferromagnet.[9] We can account for our observations by assuming that the antiferromagnetic exchange coup-

ling is sufficiently weak so that its effect can be included in an effective anisotropy field H_A. The total interaction is then of the form $2J\sum_{pairs}\vec{S}_i \cdot \vec{S}_j + \sum g\beta H_A$, where J is the ferromagnetic intralayer exchange integral. In the long-wavelength limit we calculate for the hexagonal net appropriate to our case:

$$\nu(T) = \nu(0)\left[1 - \frac{\sqrt{3}}{8\pi}\frac{kT}{JS^2}\sum_{n=1}^{\infty}\frac{1}{n}\exp\left(-\frac{ng\beta H_A}{kT}\right)\right].$$

A least squares fit of the data to this form gave $\nu(0) = 63.246$ Mc/sec $(H_{hfs} = 262\,870$ oe), $H_A = 2700$ oe, and $J = 3.95°$K. The root-mean-square deviation (0.011 Mc/sec) of the data points from the fit is within experimental error. The value of H_{hfs} is about 10% higher than that reported for $CrBr_3$, indicating, as expected, a greater delocalization of the magnetic electrons in $CrBr_3$ than in $CrCl_3$. The effective anisotropy field of 2700 oe is of the same order as the value of the magnetic dipole sum at the Cr sites, suggesting that the antiferromagnetic interlayer coupling is largely of dipolar origin. This view is also supported by the large intensity enhancement observed in this study.

[1]M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. 113, 497 (1959).
[2]C. Starr, F. Bitter, and A. R. Kaufman, Phys. Rev. 58, 977 (1940).
[3]A. M. Portis and A. C. Gossard, Suppl. J. Appl. Phys. 31, 205S (1960).
[4]N. Wooster, Z. Krist. 74, 363 (1930).
[5]W. N. Hansen and M. Griffel, J. Chem. Phys. 28, 902 (1958).
[6]J. W. Cable, M. K. Wilkinson, and E. O. Wollan, J. Phys. Chem. Solids 19, 29 (1961).
[7]R. G. Shulman, Phys. Rev. 121, 125 (1960).
[8]A. C. Gossard, V. Jaccarino, and J. P. Remeika, Phys. Rev. Letters 7, 122 (1961).
[9]J. A. Eisele and F. Keffer, Phys. Rev. 96, 929 (1954).